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THE SOLUBILITY OF PHENOL IN AQUEOUS
SOLUTIONS OF GLUCOSE, GLYCEROL,
ACETONE, AND UREA

BY

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THESIS

FOR THE


DEGREE OF BACHELOR OF SCIENCE

IN

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1926

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Irving Bancroft Morgan

ENTITLED The Solubility of Phenol in Aqueous Solutions

of Glucose, Glycerol, Acetone and Urea.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

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PART I
INTRODUCTION.

Very little has been done in determining whether mixed solutions of high concentration follow a definite solubility law. Some solutes repress the solvent power of water but being solvents in themselves, the total solubility of the solution is increased. Other solutes simply diminish the solubility of their own, the total solubility of the solution is decreased. The purpose of this problem is twofold. First to ascertain the solubility behavior of phenol in aqueous solutions of glucose, glycerol, acetone, and urea, and second, to determine if there is a similar relation between this and the solubility of benzoic and salicylic acids in like solutions.

PART II

HISTORICAL.

(1) Nernst and A. A. Noyes (2) both agreed that the concentration of molecules of a solute remains unchanged by the presence of other substances. Arrhenius (5) took exception to this and by using Noyes' own data on the solubility of thallium chloride, showed that the solvent power of a given medium was diminished by the presence of dissolved substances. This is shown conclusively in the well known commercial process of salting out. (4) A more or less accepted theory expounded by Jones and his collaborators suggested that the molecules and ions of a solute in a water solution of the solute formed hydrates and thus used up some of the water solvent, which caused a relative decrease in the solubility of the water content of the solution. (5) Smits and Maarse found that a hydrate of phenol existed and that it had a considerable range of metastable equilibrium. This not only bears out the theory of hydrate formation, but (6) carries considerable weight in the present problem. Washburn dismisses the subject briefly by stating that in working with concentrated solutions where the "thermodynamic environment" is not constant, each solution must be treated as a problem by itself and the quantitative relations connecting its properties (7) with composition must be derived by direct experiment. Lovell in working on the solubilities of benzoic and salicylic acids in aqueous solutions of glucose, glycerol, acetone, and urea, found that the organic solutes exerted a solvent action on the acids.

Also that the total solubility in all cases was found to be less than the combined solubilities of the components of the solutions acting separately. He developed an expression for the solubility in a binary medium as follows: Let A and B be two solvents where a and b represent the number of moles of each present and S the solubility. The expression then becomes $S = aS_A + bS_B - abk$.

PART III

EXPERIMENTAL

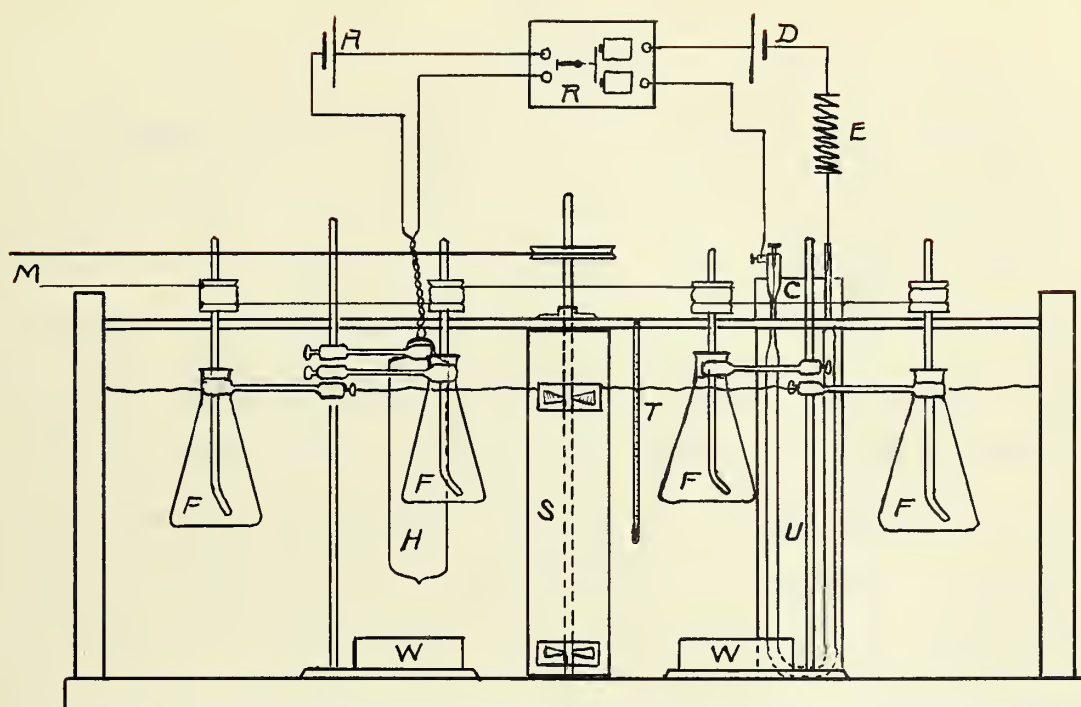
Materials - In carrying out an experiment of this nature it is necessary to have a substance of comparatively low solubility and negligible ionization in aqueous solutions. Also there must be a reasonably accurate method of determining the substance quantitatively from water solutions. Phenol satisfied all three of these conditions although the quantitative determination of it proved to be somewhat difficult. The phenol used was the crystallized product sold by the J. T. Baker Chemical Company, and had a melting point of 40.5° and a solubility of thirteen grams in one hundred grams of water. The glucose, glycerol, acetone, and urea were all of the highest grade available. Solutions of the latter were prepared of concentrations varying from 1% to 25% by weight. These solutions were only prepared as needed, as it was found that the stock solutions of glucose and glycerol could not be kept any length of time without a noticeable change due to enzyme action. The specific gravity curves were drawn from data taken from Landolt and Bornstein Tabellen.

Procedure - 200 cc. of the mixed solvent solution, i.e. 1% glucose in water, was placed in a 500 cc. Erlenmeyer flask with an excess of solid phenol. The flask was equipped with a centrifugal stirrer and placed in a thermostat carefully regulated at 25°C . Eight of these separate solutions, four

solutions in duplicate, were placed in the thermostat at one time as shown in Plate I, and stirred simultaneously for about twenty hours. The excess phenol was then allowed to separate out by standing and two 10 cc. portions of the aqueous layer removed for analysis. The quantitative procedure for determining the amount of phenol dissolved by the mixed solvent solution caused some difficulty at first. The method of adding an excess of liquid bromine to the solution was attempted, thus forming the insoluble tribromphenol. The excess bromine was determined by adding potassium iodide and titrating the iodine thus liberated with tenth normal sodium thiosulphate solution. The chief difficulty encountered with this method was the volatility of the liquid bromine. Koppenshar's modification of this method was then tried in which the original 10 cc. sample taken was diluted a thousand times and an excess of a bromide - bromate solution (2.784 grams KBrO_3 and 10 grams KBr to 1 liter) added together with 5 cc. HCl . The solution was allowed to stand until the tribromphenol had formed and settled. The excess bromine present was then determined by adding KI and titrating with tenth normal thiosulphate solution. The main difficulty in this method was the large experimental error caused by the high dilution, but this error was much smaller than that found in the first method. Because of the possible error, duplicate runs were made on each of the solvent solutions and check determinations were made of the phenol dissolved in each of the duplicate samples. The average of the four determinations

thus made on one mixed solution of a certain concentration was taken as the amount of phenol dissolved in a solution of that concentration.

Plate I



ARRANGEMENT OF APPARATUS IN THERMOSTAT.

- F - Flasks for Solutions
- S - Stirrer for Thermostat
- H - Heater for Thermostat
- M - Belts Connected to Motor
- U - Mercury Column Regulator
- C - Platinum Contact Point.
- A - Source of 110 A.C. Current.
- D - Source of 12 D.C. Current.
- R - Relay
- E - Rheostat
- W - Weights

PART IV

RESULTS

Glucose - The results of the solubility of phenol in glucose water solutions are tabulated in Table I and the graphical representation is given in Plate III. The black line shows the solubility of phenol in glucose-water solutions in grams per 100 grams of solution, while the red line shows the calculated solubility of phenol in the water present in 100 grams of the glucose-water solutions. Because of the dilution to which the phenol solution is subjected during the process of determining the amount of phenol which went into solution, a slight experimental error will produce a very appreciable discrepancy in the final result. For example, 0.1 cc. difference in the amount of the thiosulphate solution used in titrating the excess of bromine added will produce a difference of 0.4 grams in the weight of phenol found to be present. The results have therefore been interpreted to mean that the black and red lines should practically coincide on the graph. In other words the presence of glucose lowers the solubility of the solution but does not alter the solvent power of the water present. An alternate explanation would be that the solubility of the phenol in the glucose hydrate is the same as that of water.

TABLE I

The Solubility of Phenol in Glucose Solutions.

% Glucose	Sp.Gr.	Grams phenol/100 gms. sol.	Gms. Phenol dissolved in water present in 100 gms. of solution.
0	1.0000	13.001	13.001
1	1.0027	12.633	12.871
5	1.0171	12.122	12.351
10	1.0379	11.770	11.700
15	1.0585	11.393	11.051
20	1.0793	10.488	10.401
25	1.1000	9.448	9.751

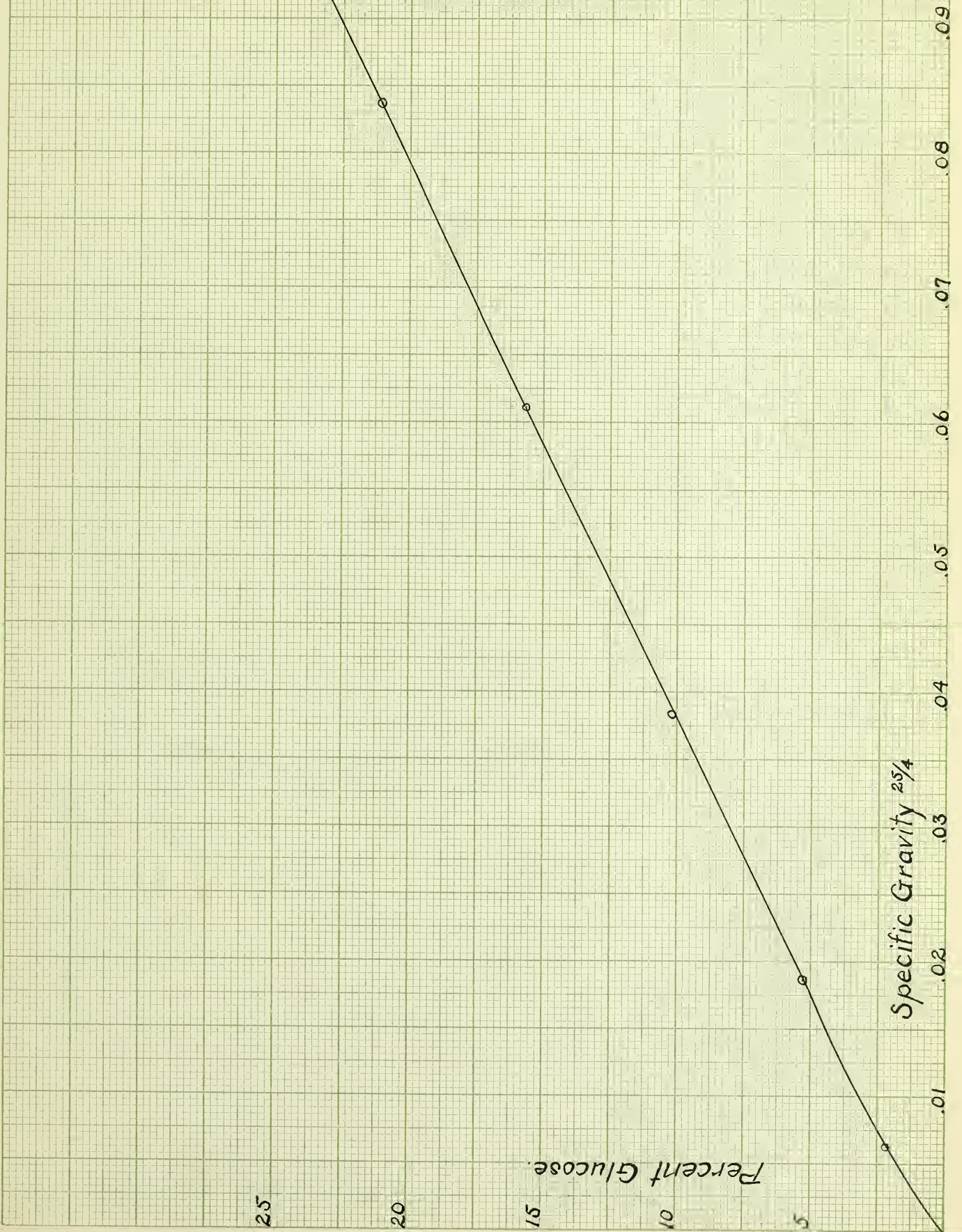
Glycerol - Table II and Plate V show the solubility of phenol in glycerol-water solutions. In this case as before, the red line represents the solubility of phenol in the water present in 100 grams of solution and is the same in the case of glucose since it is a function of the percent water present in the solution. However, the black curve representing the solubility in grams per 100 grams of solution shows a marked deviation from the similar curve for glucose. The solubility increases with an increase in the percentage glycerol present. This increase in the solubility is comparatively small in low concentrations, but increases very rapidly above 15%. This shows that glycerol solutions are better solvents for phenol than those of glucose, and leads to the belief that glycerol itself has a specific solubility for phenol. This increase in solubility, due to the presence of glycerol cannot be assumed to be additive as the solubility curve is not a straight line.

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SPECIFIC GRAVITY CURVE FOR VARYING PERCENTS OF GLUCOSE IN WATER.



SOLUBILITY OF PHENOL IN VARYING PERCENT SOLUTIONS OF GLUCOSE.

25

20

15

10

5

Percent Glucose

Grams Per 100 Grams Solution. —

Grams Dissolved By H_2O Present
in 100 Grams of Solution. —

Grams Phenol Dissolved.

2

4

6

8

10

12

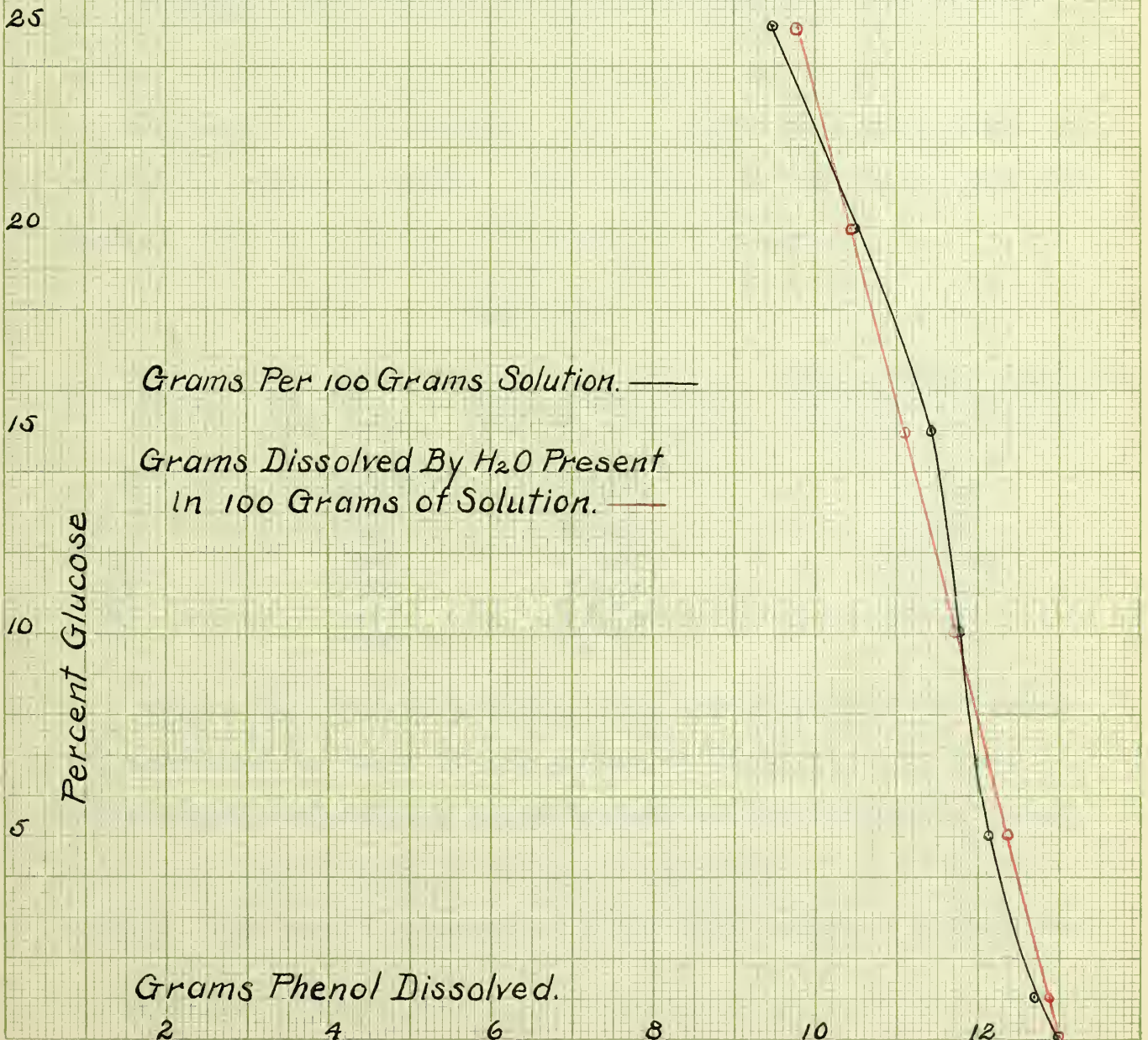


TABLE II

% Glycerol	Sp. Gr. from curve	Gms. phenol per 100 gms. solution	Gms. phenol dissolved in water present in 100 gms. solution.
0	1.0000	13.001	13.001
1	1.0006	13.387	12.871
5	1.0080	14.065	12.351
10	1.0206	14.890	11.701
15	1.0360	17.566	11.051
20	1.0514	27.603	10.401
25	1.0617	51.236	9.751

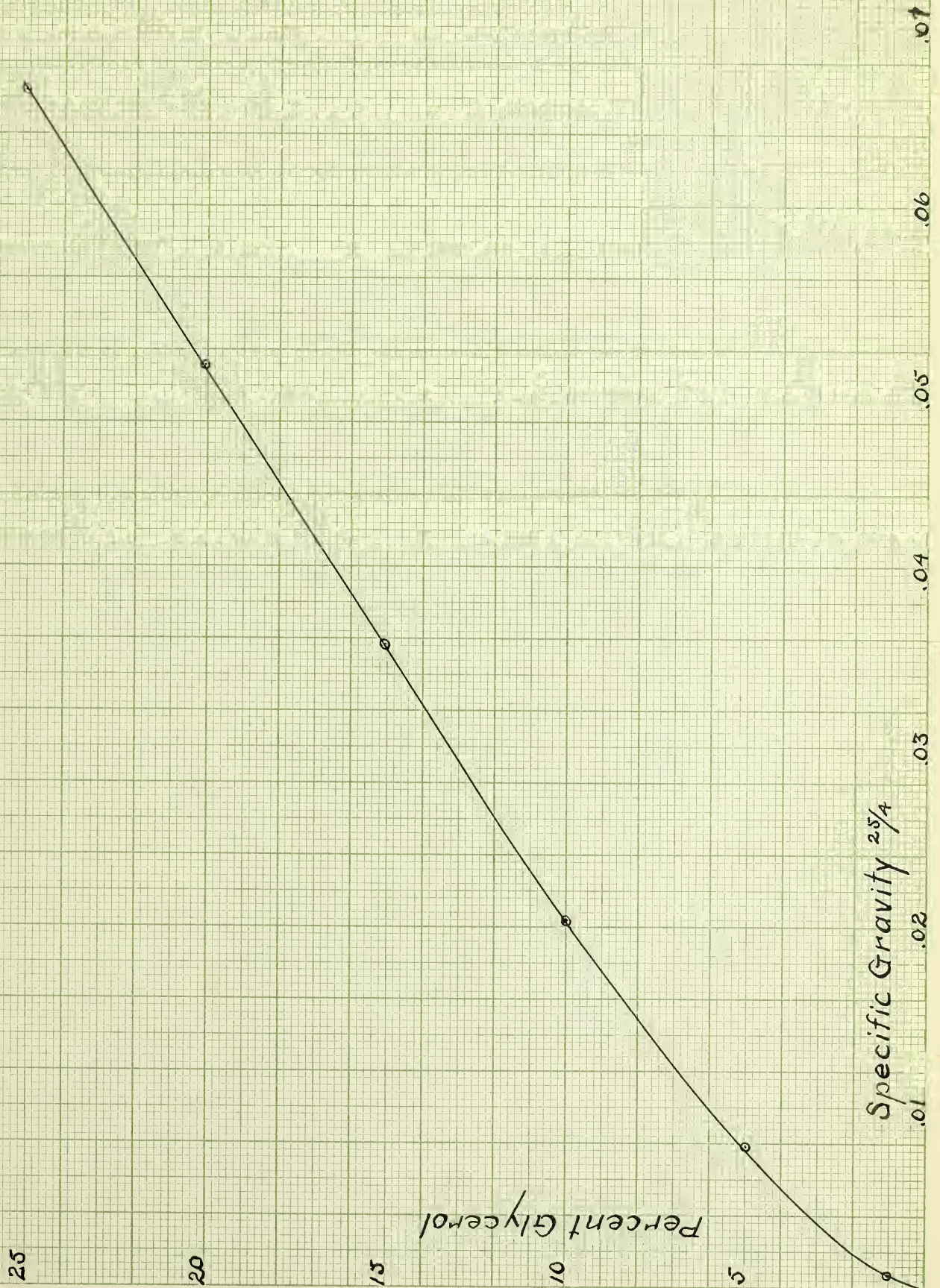
Acetone - The results of the determinations with acetone-water solutions are given in table III and Plate VII. The solubility of phenol showed a very marked decrease in solubility in solutions up to 5% acetone, but at higher concentrations the solubility became constant. The decrease in solubility was much greater than that in the glucose-water solutions.

TABLE III

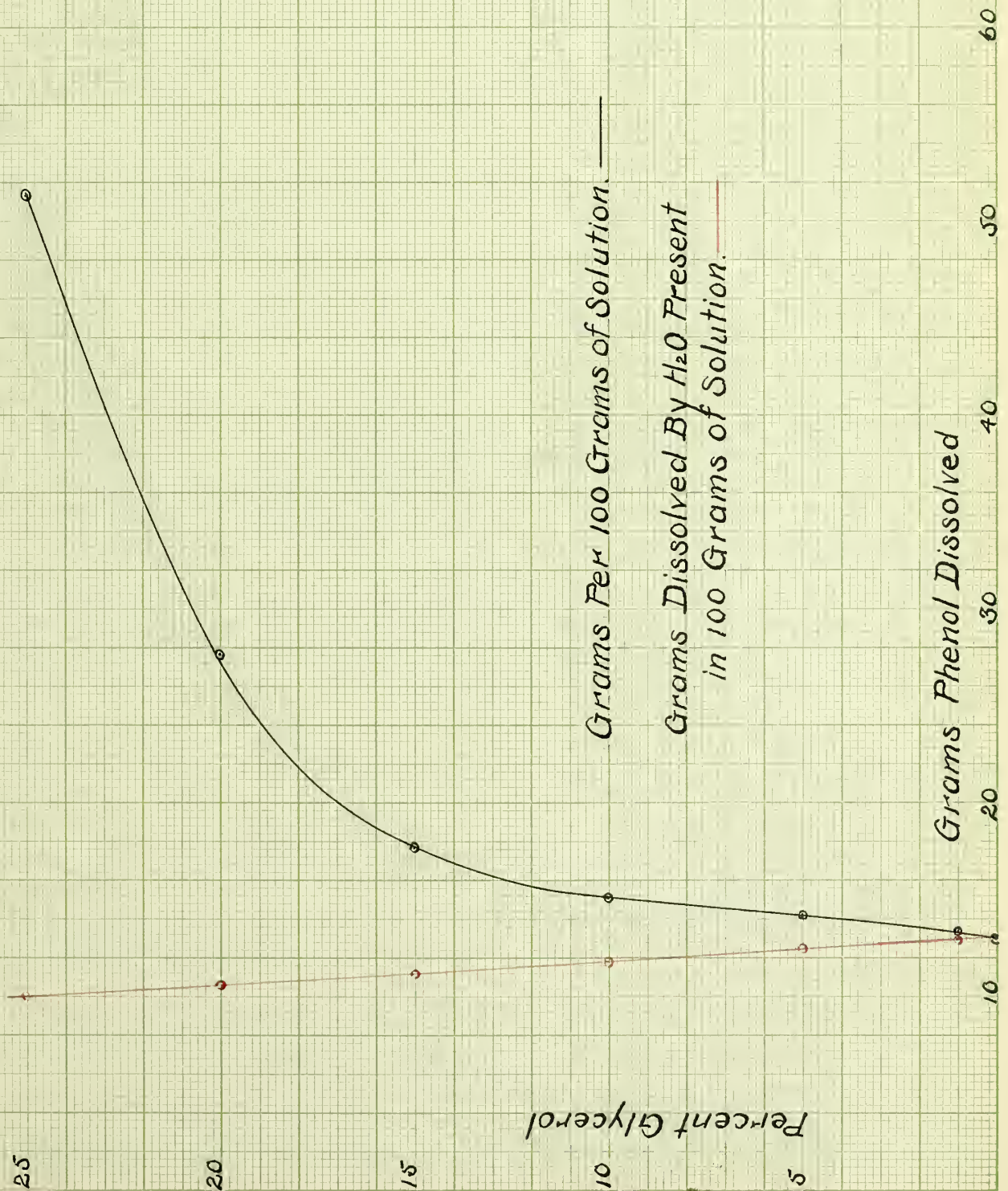
% Glycerol	Sp. gr. from curve	Gms. phenol per 100 gms. solution	Gms. phenol dissolved in water present in 100 gms. solution.
0	1.0000	13.001	13.001
1	.998	11.691	12.871
5	.992	8.233	12.351
10	.985	8.083	11.700
15	.976	8.137	11.051
20	.969	8.175	10.401
25	.962	8.275	9.751

Urea - The results obtained from the urea-water solutions are tabulated in Table IV and plotted on Plate IX. The urea increased the solubility of the phenol in the urea-water solutions in a manner similar to that of glycerol. In this case however, the marked increase did not occur until a 20% concen-

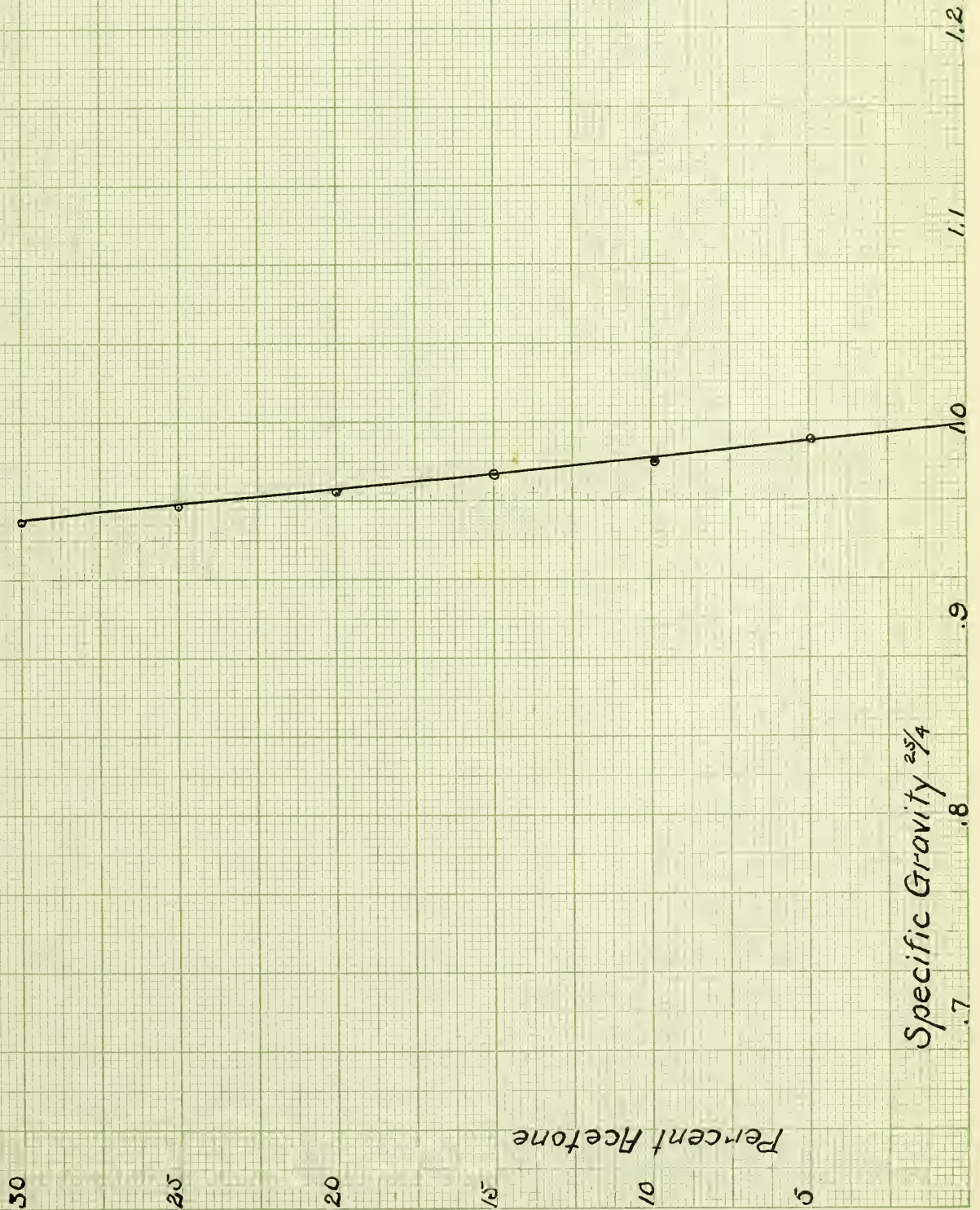
SPECIFIC GRAVITY CURVE FOR VARYING PERCENTS OF GLYCEROL IN WATER.



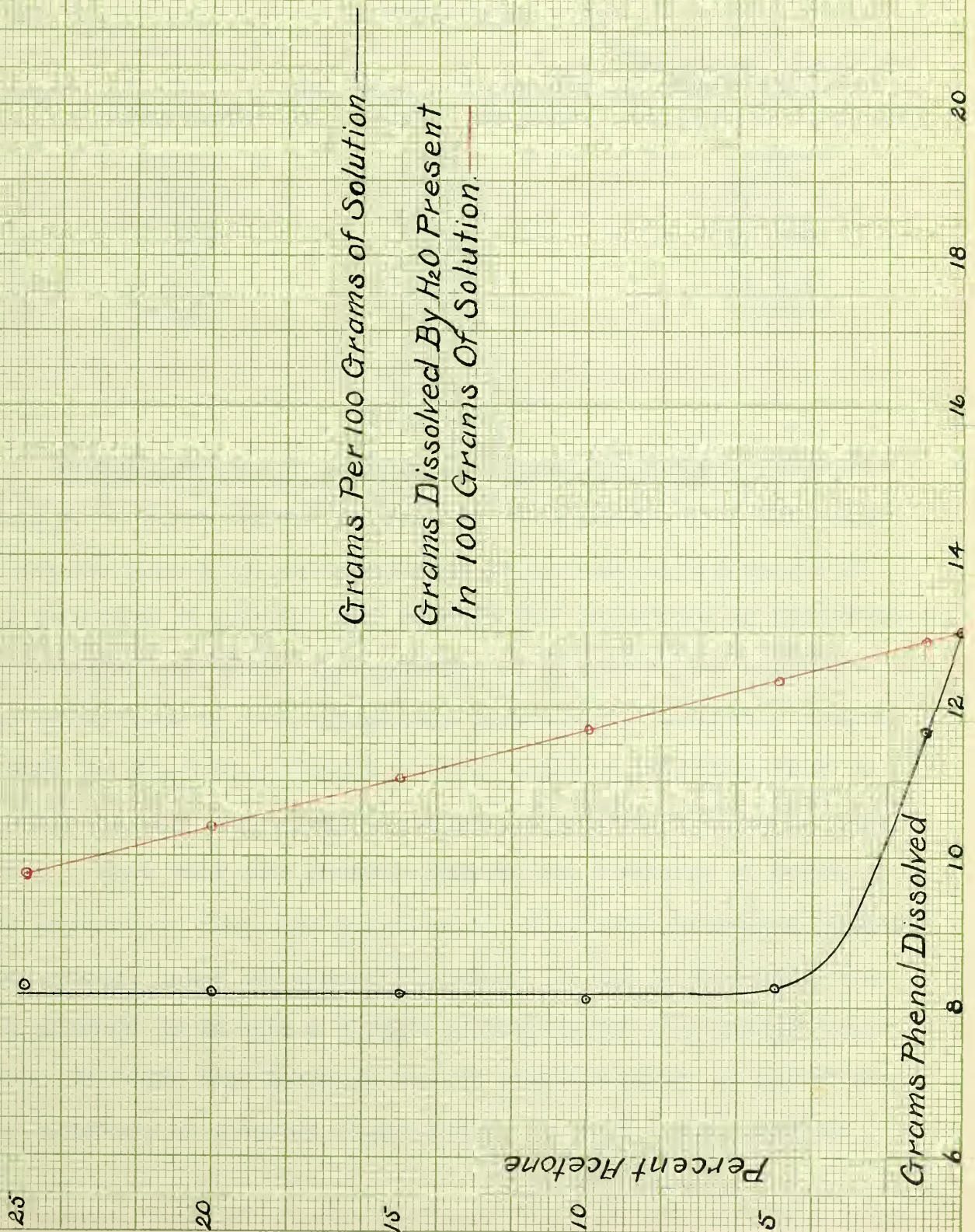
SOLUBILITY OF PHENOL IN VARYING PERCENT SOLUTIONS OF GLYCEROL.



SPECIFIC GRAVITY CURVE FOR VARYING PERCENTS OF ACETONE IN WATER.



SOLUBILITY OF PHENOL IN VARYING PERCENT SOLUTIONS OF ACETONE.



tratruration was reached, while with glycerol the greater increase occurred above 15% concentration.

TABLE IV.

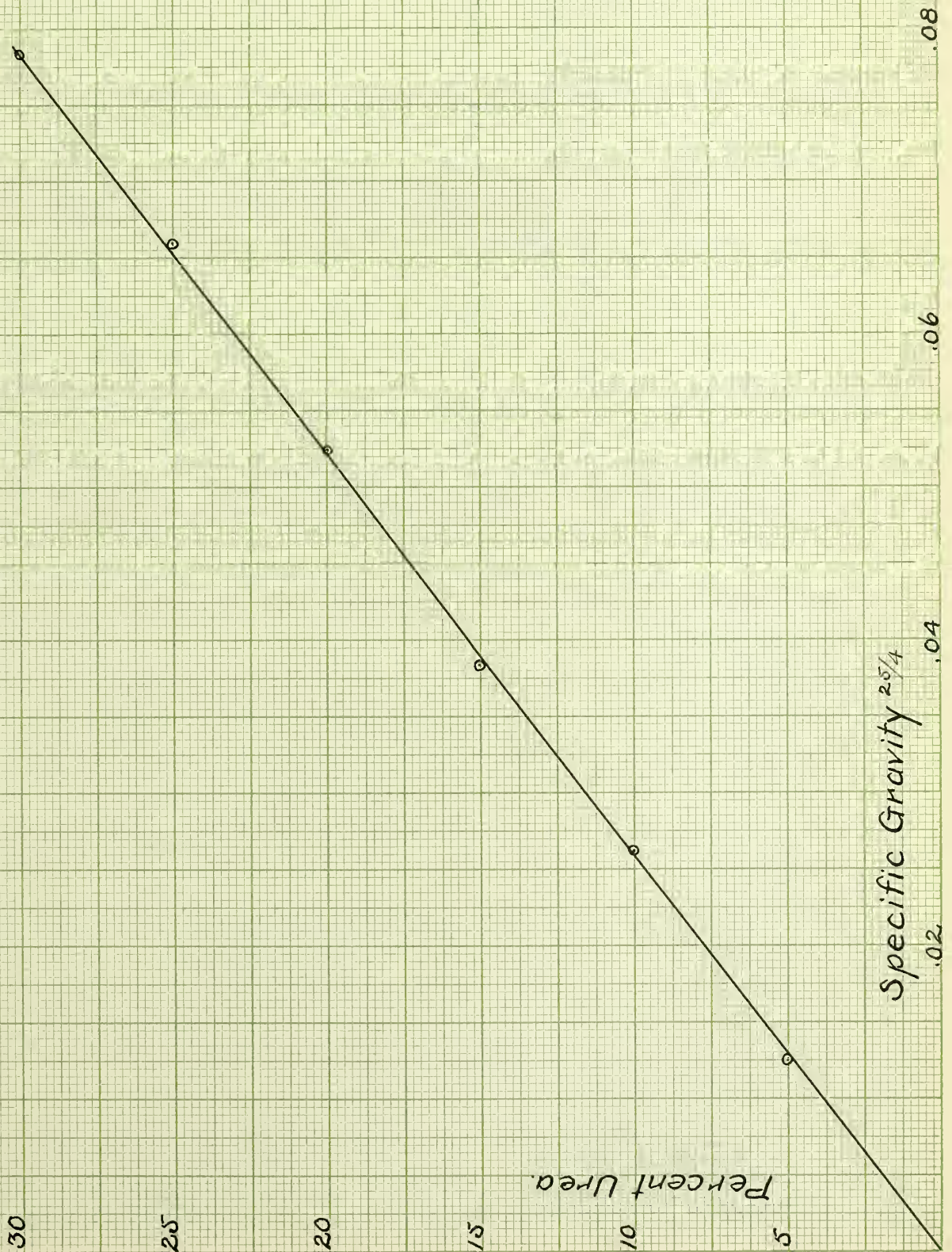
% urea	Sp. Gr. from curve	Gms.phenol dissolved in 100 gms. solution	Gms.phenol dissolved in water present in 100 gms. of solution
0	1.0000	13.001	13.001
1	1.0025	13.208	12.871
5	1.0125	14.874	12.351
10	1.0265	16.257	11.700
15	1.0380	19.402	11.051
20	1.0525	21.047	10.401
25	1.0660	39.569	9.751

PART V

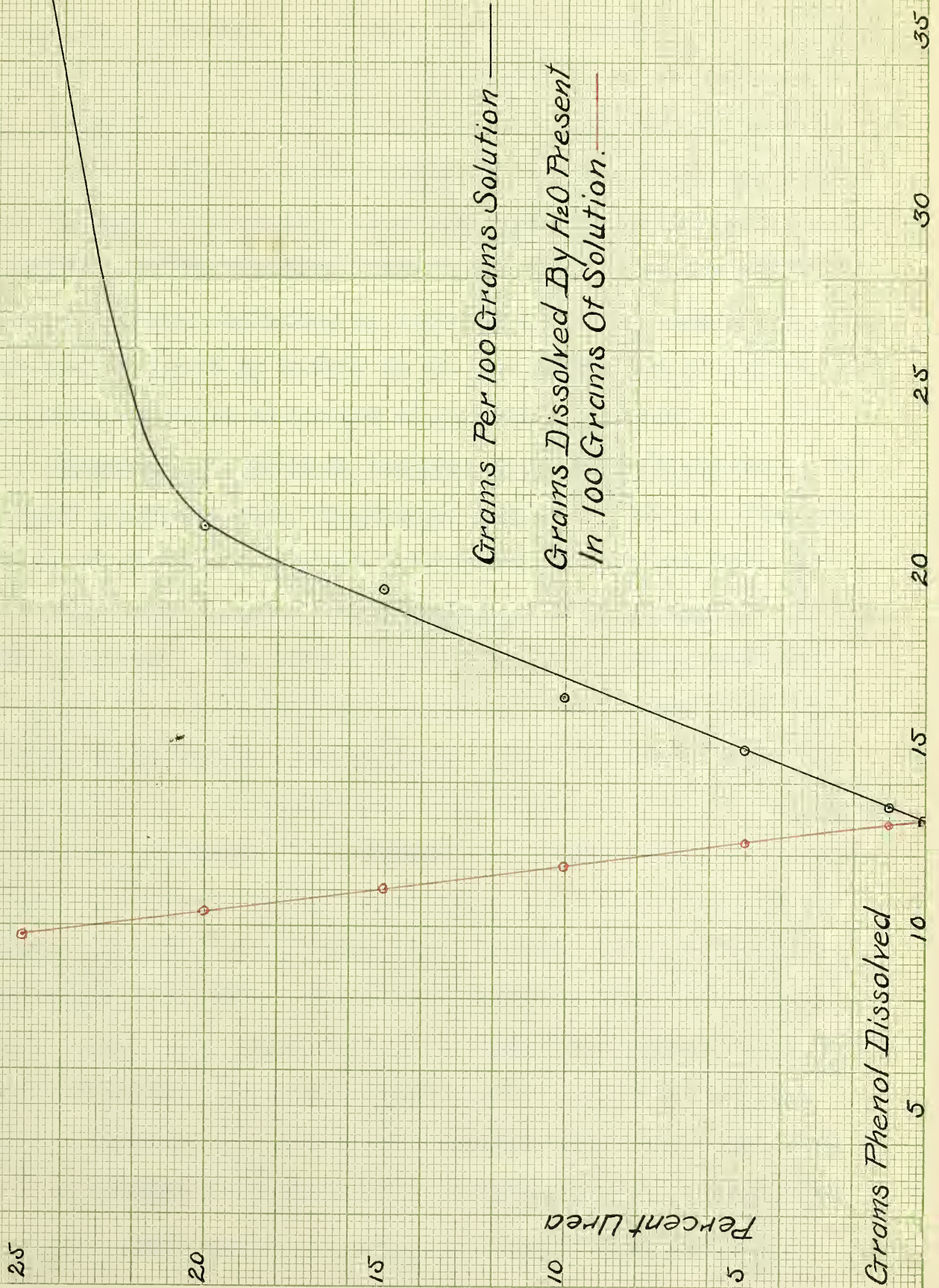
DISCUSSION.

Solvent Action of Organic Compounds on Phenol - From the results of these determinations it is apparent that the solubility of phenol in mixed aqueous solutions is decreased by the presence of glucose and acetone and increased by the presence of glycerol and urea. In the case of glucose, the decrease in the solubility of the phenol was practically inversely proportional to the concentration of the solution, showing that the glucose neither repressed or aided the solvent action of the water. This does not exactly follow the theories of Noyes and Arrhenius, that the presence of dissolved molecules reduces the solvent power of water. However, it may be possible that the glucose alone has a slight solvent power for phenol which would overcome any decrease in the solvent power of water that the presence of glucose might incur. Lovell found similar

SPECIFIC GRAVITY CURVE FOR VARYING PERCENTS OF UREA IN WATER.



SOLUBILITY OF PHENOL IN VARYING PERCENTS SOLUTIONS OF UREA.



conditions existing in the solubility of benzoic and salicylic acids in glucose solutions. The solubility of the two acids was decreased, but there was a slightly higher solubility in the solution than in the water present in an equivalent amount of solution. The glycerol and urea produced an increase in the solubility of the phenol. This shows that glycerine and urea exert a solvent influence on the phenol. These again are like the results found by Lovell as to the solubility of benzoic and salicylic acids in solutions of glycerol and urea.

Formation of Addition Product in Acetone Solutions - The acetone solutions gave remarkably peculiar results. The solubility of the phenol in the acetone-water solution fell far below the solubility of the phenol in the water present in the same solution. The solubility finally became constant above 5% solutions. With similar solutions Lovell found that the solubility of benzoic and salicylic acids increased with an increase in the concentration of acetone. In the case of phenol, therefore, presuming there should be a similarity for all solutions, an addition product must have been formed between the phenol and acetone, or there was a marked hydration between the phenol and water. The latter does not seem reasonable, since there is no difficulty of a like nature experienced with any of the other organic solutes used. Schmidlin and Lang⁽⁸⁾ found a compound of acetone and phenol which was in the form of long needles melting at 15°C. There being no better name available, they called it Phenol-acetone. This assists in

bearing out the assumption of an addition product being formed. Another reason for assuming the formation of the so called phenol acetone can be found by means of the Phase rule. The solution has one degree of freedom (F), that of temperature, and consists of three components (C) namely, water, acetone, and phenol. By substituting in the general phase rule formula $F = C - 2 - P$ and solving for the number of phases present, (P) it is found that there should be four phases present. Only three of these phases can be accounted for, the vapor phase, the solution phase, and the phenol phase. It can be assumed therefore, that the fourth phase must be some combination of the phenol and acetone. Also according to the above phase rule conditions the concentration of the phenol in solution should remain, which it does, as can be seen from the fact that the curve is perfectly vertical above 5% acetone.

Group Influences - In making a comparison of group influences or the effects of certain groups on organic solvents, it was found that OH groups apparently reduced the solubility. Phenol, benzoic acid, and salicylic acid all showed lower solubility in glucose solutions than in glycerol and the former has many more OH groups than glycerol. The CH_3 group in the acetone aided the solubility of the benzoic and salicylic acids, but due to the formation of the addition product between phenol and acetone, the actual solubility of phenol in acetone solutions was not obtained and consequently a comparison with phenol

cannot be made in this case. The CO group exerted no apparent influence on the solubility of any of the compounds used and therefore it is concluded that this group does not have any active influence on the solubility. However, the NH_2 groups have quite a noticeable effect on the solubility. The phenol, benzoic acid, and salicylic acid were all more soluble in urea-water solutions than in any other of the mixed solutions.

PART V

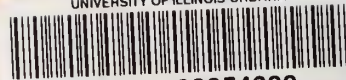
SUMMARY

1. The solubility of phenol has been determined at 25° in solutions of glucose, glycerol, acetone, and urea varying from 1-25% by weight.
2. These solutes with the exception of glucose and acetone have a solvent action on phenol.
3. The formation of an addition product with phenol in acetone solution was shown.
4. A comparison was made of the solubility of phenol with benzoic and salicylic acids in the same kind of solutions.
5. A comparison was made of the group influences on the solubility of phenol, benzoic acid, and salicylic acid.

PART VIII
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